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(54) Title: LUBRICANTS WITH SUSTAINED FUEL ECONOMY PERFORMANCE

(57) Abstract

A lubricant composition comprising a major amount of a lubricant base oil, and a minor amount of additives comprising (A) oxymolybdenum dithiocarbamate sulphide having a specific structure, (B) zinc dialkyldithiophosphate having a specific structure, (D) an ashless dispersant, (E) a boron containing additive which may be the ashless dispersant or another additive, and (F) a metal detergent, wherein to the total weight of the composition, the molybdenum content from oxymolybdenum dithiocarbamate sulfide is at 200 to 2,000 ppm; the phosphorous content from zinc dialkyldithiophosphate is at 0.02 to 0.15 % by weight; the sulfur content from sulfur compounds is at 0.02 to 0.30 % by weight; the content of a metal detergent is at 1 to 10 % by weight; and the boron content is at 0.005 to 0.06 % by weight. The lubricant composition of the present invention has excellent low abrasion properties and can sustain good friction properties while exhibiting resistance to oxidation at higher temperatures in the presence of gaseous nitrogen oxides. The lubricant composition of the present invention is used preferably as a crankcase lubricants for internal combustion engines.

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Lubricants with Sustained Fuel Economy Performance

Field of the Invention

The present invention relates to a novel lubricant composition.

5 More specifically, it relates to a lubricant composition having good low abrasion and friction properties and being capable of sustaining low friction over a long period of time with no deterioration even in an atmosphere containing gaseous nitrogen oxides. The lubricant composition can be used in internal combustion engine crankcases,

10 automatic transmissions, wet brakes and power steering. Preferably it is used in crankcases of internal combustion engines.

Background of the Invention

Lubricants have been used to lubricate internal combustion engines, driving systems such as automatic transmission, wet brakes and power steering, and gears. Lubricants for internal combustion engines in particular have as their primary function lubricating various sliding parts such as piston rings and cylinder liners, crankshaft bearings and connecting rod, and valve operating parts. Beyond this primary function crankcase lubricants also serve to cool the inside of engines, to clean engine parts, to disperse combustion products, and further to prevent rust and corrosion.

In recent years internal combustion engines have been modified to lower fuel consumption while increasing power output and improving durability even under severe operating conditions. In consequence greater demands have been placed on lubricants. In addition, combustion gases from internal combustion engines leak from between the piston and the cylinder into the crankcase in the form of blow-by-gas. These combustion gases contain higher levels of gaseous nitrogen oxides, which together with oxygen in the blow-by-gas deteriorate the lubricants. The levels of gaseous nitrogen oxides leaking into the crankcase tend to increase as engine performance demands increase. To prevent deterioration in an atmosphere containing gaseous nitrogen oxides, while retaining lubricity performance, lubricants are blended with various additives, for example, wear preventing agents, metal salts of

organic acids commonly known as detergents, ashless dispersants, and antioxidants.

5 Engine lubricating parts are mostly in a state of fluid lubrication, but vertical dead centers of valve operating systems and pistons are likely in a state of interface (or boundary) lubrication. In such a state of interface lubrication, wear preventing properties are generally provided by adding zinc dithiophosphate.

10 Friction modifiers are also added to the lubricants as a countermeasure to decrease efficiency loss from friction and thereby reduce fuel consumption. As such friction modifiers, for example, organic molybdenum compounds, fatty acid esters, alkylamines and the like, are used in general.

15 After intensive investigations under such circumstance, it has been found that friction modifiers are effective in a fresh lubricant, that is, at the initial stage of use after their addition, but friction modifiers lose their effect when they are oxidized and deteriorated by atmospheric oxygen, and that the decrease of the efficacy is distinctive in the presence of gaseous nitrogen oxides. Thus, the present invention has been achieved for the purpose of developing a lubricant composition which can provide 20 sustained fuel economy performance with the effect of decreasing friction in engines for a long period of time in the presence of gaseous nitrogen oxides.

Summary of the Invention

25 A lubricant has been discovered that has good lubricity and resistance to deterioration in the presence of oxygen and gaseous nitrogen oxides. It comprises a major amount of a lubricant base oil, a basestock of lubricating viscosity, to which a minor amount of additives has been added. The additives comprise specific amounts of oxymolybdenum dithiocarbamate sulfide having specific alkyl groups, zinc 30 dialkyldithiophosphate having specific alkyl groups, one or more specific sulfur containing compounds, an ashless dispersant and a boron containing additive which may be the ashless dispersant. In further

aspects of the invention a metal detergent is used. Conveniently, the dispersant and boron are added as a borated succinimide. Thus, the present invention has been achieved on the basis of the finding.

The present invention is a lubricant composition comprising a major amount of a lubricant base oil having added thereto a minor amount of additives comprising (A) oxymolybdenum dithiocarbamate sulfide having alkyl groups with 8 to 18 carbon atoms, (B) zinc dialkyldithiophosphate having primary alkyl groups with 1 to 18 carbon atoms, (C) one or more additional peroxide decomposing sulfur compounds, (D) an ashless dispersant, and (E) a boron containing additive in an amount sufficient to provide at from 0.005 to 0.06 % by weight boron to the finished lubricant wherein to the total weight of the composition, the molybdenum content from oxymolybdenum dithiocarbamate sulfide is at 200 to 2,000 ppm (ratio by weight); the phosphorous content from zinc dialkyldithiophosphate is at 0.02 to 0.15 % by weight; and the sulfur content from the additional peroxide decomposing sulfur compound is at 0.02 to 0.30 % by weight. Conveniently, the additional peroxide decomposing sulfur compound is selected from the group consisting of zinc dialkyldithiocarbamate, copper dialkyldithiocarbamate or nickel dialkyldithiocarbamate wherein the dialkyldithiocarbamate has alkyl groups with 2 to 18 carbon atoms, bis(dialkylthiocarbamoyl)disulfide having an alkyl group with 2 to 18 carbon atoms, disulfide having an alkyl group with 2 to 18 carbon atoms, disulfide having an allyl group, an alkylallyl group or an allylalkyl group, with 6 to 18 carbon atoms, olefin sulfide, fish oil sulfide, whale oil sulfide and mixtures of the any of the foregoing.

In a further aspect, the lubricant also comprises (F) from 1 to 10 % by weight of one or more metal detergents selected from the group consisting of calcium salicylate, magnesium salicylate, calcium sulfonate, magnesium sulfonate and calcium phenate. Conveniently the metal detergent is added at level providing from 0.5 to 8 percent by weight on an active ingredient basis. One lubricant within the present invention includes from 1.75 to 4 wt % (active ingredient basis) of calcium salicylate.

Conveniently, the lubricant comprises an oil of lubricating viscosity having added thereto (A) oxymolybdenum dithiocarbamate sulfide having alkyl groups which may be the same or different with 8 to 18 carbon atoms, (B) zinc dialkyldithiophosphate having primary alkyl groups with 1 to 18 carbon atoms, and (C) one or more additional sulfur compounds selected from the group consisting of zinc dialkyldithiocarbamate, copper dialkyldithiocarbamate or nickel dialkyldithiocarbamate wherein the dialkyldithiocarbamate has alkyl groups with 2 to 18 carbon atoms, bis(dialkylthiocarbamoyl)disulfide having an alkyl group with 2 to 18 carbon atoms, disulfide having an alkyl group with 2 to 18 carbon atoms, disulfide having an allyl group, an alkylallyl group or an allylalkyl group, with 6 to 18 carbon atoms, olefin sulfide, fish oil sulfide and whale oil sulfide, (D and E) boron containing succinimide, and (F) one or more metal detergents selected from the group consisting of calcium salicylate, magnesium salicylate, calcium sulfonate, magnesium sulfonate and calcium phenate, wherein to the total weight of the composition, the molybdenum content from oxymolybdenum dithiocarbamate sulfide is at 200 to 2,000 ppm (ratio by weight); the phosphorous content from zinc dialkyldithiophosphate is at 0.02 to 0.15 % by weight; the sulfur content from the additional sulfur compounds is at 0.02 to 0.30 % by weight; the content of a metal detergent is at 1 to 10 % by weight; and the boron content from boron containing succinimide is at 0.005 to 0.06 % by weight.

Methods to determine the amount of molybdenum, phosphorus, boron, nitrogen, and sulfur are well known in the art. For example molybdenum, phosphorus, and boron can all be determined by inductively coupled plasma atomic emission spectrometry, JPI-5S-38-92. Nitrogen may be determined by the chemiluminescence method described in JIS K 2609 7. Sulfur may be determined by the method described in ASTM D 5453 which involves converting sulfur to sulfur dioxide, exciting the sulfur dioxide with ultraviolet light and measuring the amount of fluorescent emission produced.

Detailed Description

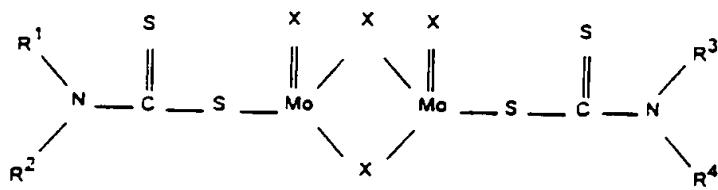
As the lubricant basestock to be used in the lubricant composition of the present invention, use may be made of those base oils conventionally used, for example, mineral oils and synthetic oils, without any specific limitation.

Thus suitable mineral oils include those made from raffinate produced by solvent purification of a lubricant raw material with an aromatic extraction solvent such as phenol and furfural, hydrogenation processed oils by hydrogenation processing with a hydrogenation catalyst such as cobalt and molybdenum on the carrier silica-alumina, or mineral oils such as lubricant distillate produced by wax isomerization, for example, 60 Neutral Oil, 100 Neutral Oil, 150 Neutral Oil, 300 Neutral Oil, 500 Neutral Oil, and Bright Stock.

Alternatively, suitable synthetic oils include, for example, poly- α -olefin oligomers, polybutene, alkylbenzene, polyol ester, polyglycol ester, dibasic acid ester, phosphate ester, silicon oil and the like. These may be used singly or in combination with two or more, or a mineral oil may be mixed with a synthetic oil for use.

The base oil to be used in the lubricant composition of the present invention has a viscosity at 100°C in the range of 3 to 20 cSt. Particularly, preference is given to a hydrogenation decomposition oil and a wax isomerization oil, with 3 % by weight or less of aromatic components, 50 ppm or less of sulfur components and 50 ppm or less of nitrogen components.

As the oxymolybdenum dithiocarbamate sulfide to be blended with the lubricant composition of the present invention, use is made of a compound represented by the general formula (1):



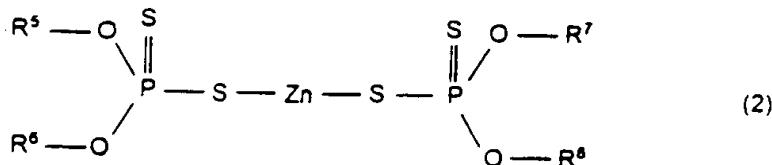
(1)

wherein R¹, R², R³ and R⁴ may be the same or different, each representing an alkyl group with 8 to 18 carbon atoms; and x represents S or O.

The alkyl group with 8 to 18 carbon atoms, represented by R¹, R², R³ and R⁴ in the general formula (1), may be linear or branched. For the lubricant of the present invention, the carbon number of the alkyl group represented by R¹, R², R³ and R⁴ is most preferably 8 to 13. Specific examples of the alkyl group, represented by R¹, R², R³ and R⁴, include 2-ethylhexyl, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group and octadecyl group.

In the lubricant composition of the present invention, one species of oxymolybdenum dithiocarbamate sulfide may be used or two or more species thereof may be used in combination. Furthermore, oxymolybdenum dithiocarbamate sulfide is blended so that the molybdenum content from oxymolybdenum dithiocarbamate sulfide in the finished lubricant is from about 200 to about 2,000 ppm (ratio by weight), preferably 300 to 800 ppm (ratio by weight) to the total weight of the composition. When oxymolybdenum dithiocarbamate sulfide is blended in an amount such that the molybdenum content from oxymolybdenum dithiocarbamate sulfide is below 200 ppm (ratio by weight) to the total weight of the composition, the effect of improving the friction properties (low friction) is not satisfactorily exhibited; and when oxymolybdenum dithiocarbamate sulfide is blended at an amount such that the molybdenum content from oxymolybdenum dithiocarbamate sulfide is above 2,000 ppm (ratio by weight) to the total weight of the composition, the improvement of the effect is not observed in proportion to the amount, and sludge is likely to be caused. Oxymolybdenum dithiocarbamate sulfides are well known and available commercially. Representative methods for their preparation are described in US 4,098,705.

As the zinc dialkyldithiophosphate to be blended with the lubricant composition of the present invention, us is made of a compound represented by the general formula (2):



wherein R⁵, R⁶, R⁷ and R⁸ may be the same or different, each representing a primary alkyl group with 1 to 18 carbon atoms. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more primary alcohol with P₂S₅ and then neutralizing the formed DDPA with a zinc compound. To make the zinc salt, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to use of an excess of the basic zinc compound in the neutralization reaction. In order to obtain oil solubility, the total number of carbon atoms in the alcohols reacted to form the dithiophosphoric acid will generally be about 5 or greater.

The primary alkyl group represented by R⁵, R⁶, R⁷ and R⁸ in the general formula (2), may be in a linear chain or in a branched chain, including for example methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group and octadecyl group. In the lubricant composition of the present invention, preferably, use may be made of zinc dialkyldithiophosphate having a primary alkyl group with 3 to 12 carbon atoms.

In the lubricant composition in accordance with the present invention, zinc dialkyldithiophosphate is blended so that the phosphorous content from zinc dialkyldithiophosphate is at 0.02 to 0.15 % by weight, preferably 0.04 to 0.12 % by weight to the total weight of the composition. When zinc dialkyldithiophosphate is blended at an amount such that the phosphorous content from zinc dialkyldithiophosphate is below 0.02 % by weight to the total weight of the composition, the resulting composition cannot get satisfactory wear performance or cannot get a small coefficient.

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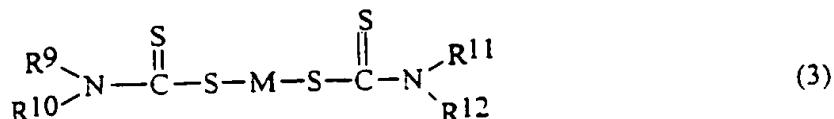
of friction satisfactory under the operation conditions of high oil temperature and low-speed rotation; and when zinc dialkyldithiophosphate is blended at an amount such that the phosphorous content from zinc dialkyldithiophosphate is above 0.15 % by weight to the total weight of the composition, the improvement of the effect is not observed in proportion to the amount.

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The additional sulfur compound required for the present invention is selected from any of the sulfur compounds that efficiently decompose peroxides. Without intending to be bound by any theory, the extended fuel economy performance of the present invention may be attributable to suppressed consumption of the oxymolybdenum dithiocarbamate sulfide and the zinc dialkyldithiophosphate because the sulfur compounds efficiently decompose peroxides.

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As the dialkyldithiocarbamate salt to be blended in the lubricant composition of the present invention, use is made of a compound represented by the general formula (3)



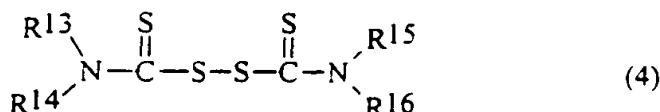
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wherein M represents zinc, copper or nickel; R⁹, R¹⁰, R¹¹ and R¹² may be the same or different, each representing an alkyl group with 2 to 18 carbon atoms. Metal salts of dialkyldithiocarbamic acid are well known and readily available. Processes for their synthesis are described in US 4,623,473 and 4,740,322.

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The alkyl group of 2-18 carbon atoms represented by R⁹, R¹⁰, R¹¹ and R¹² in the general formula (3) may be linear or branched, including for example ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group and octadecyl group.

As the bis(dialkylthiocarbamoyl)disulfide to be blended in the lubricant composition of the present invention, use may be made of a compound represented by the general formula (4):



5 wherein R₁₃, R₁₄, R₁₅ and R₁₆ may be the same or different, each
representing an alkyl group with 2 to 18 carbon atoms. The alkyl group of
2-8 carbon atoms represented by R₁₃, R₁₄, R₁₅ and R₁₆ in the general
formula (4) may be linear or branched, including for example ethyl group,
propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl
group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl
group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl
group and octadecyl group.

As the disulfide to be blended in the lubricant composition of the present invention, use is made of a compound represented by the general formula (5):



wherein R¹⁷ and R¹⁸ may be the same or different, each representing an alkyl group with 2 to 18 carbon atoms or an allyl group, an alkylallyl group or an allylalkyl group, with 6 to 18 carbon atoms. The alkyl group of 2-8 carbon atoms represented by R¹⁷ and R¹⁸ in the general formula (5) may be linear or branched, including for example ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group and octadecyl group; the allyl group, the alkylallyl group or the allylalkyl group, having 6 to 18 carbon atoms and being represented by R¹⁷ and R¹⁸, includes for example phenyl group, benzyl group, phenetyl group, methylbenzyl group, diphenylmethyl group and the like.

Olefin sulfide, fish oil sulfide and whale oil sulfide, to be blended with the lubricant composition of the present invention, should be olefin sulfide (polysulfide) being produced by sulfide processing of polymers such as isobutylene and having a sulfur content of 25 to 40 % by weight, 5 fish oil sulfide and whale oil sulfide produced by processing individually fish oil and whale oil in the same manner.

In the lubricant composition of the present invention, the metal dialkyldithiocarbamate represented by the general formula (3), bis(dialkylthiocarbamoyl)disulfide represented by the general formula (4), 10 disulfide represented by the general formula (5), olefin sulfide, fish oil sulfide and whale oil sulfide, may be used singly or in combination of two or more thereof. These sulfur compounds may be blended so that the sulfur content derived from these added sulfur compounds is 0.02 to 0.30 % by weight. When these sulfur compounds are blended at an amount 15 such that the sulfur content from these added sulfur compounds is below 0.02 % by weight to the total weight of the composition, the effect of sustaining friction decrease is insufficient; when these sulfur compounds are blended at an amount such that the sulfur content from these sulfur compounds is above 0.30 % by weight to the total weight of the 20 composition, the improvement of the effect cannot be brought about in proportion to the amount.

If desired, one or two or more metal detergents selected from the group consisting of calcium salicylate, magnesium salicylate, calcium sulfonate, magnesium sulfonate, and calcium phenate may be blended 25 with the lubricant composition of the present invention. These metal detergents may be blended at 1 to 10 % by weight to the total weight of the composition. When these metal detergents are blended below 1 % by weight to the total weight of the composition, the cleansing effect is unsatisfactory; when these metal detergents are blended above 10 % by 30 weight to the total weight of the composition, the improvement of the effect cannot be observed in proportion to the amount, or rather, ash content may increase. Recognizing that metal detergents comprise oil suspensions of neutral and overbased metal salts of organic acids, the

treat rates recited correspond to treat rates of from about 0.5 to 8 weight percent active ingredient.

Metal-containing or ash-forming detergents generally comprise a polar head with a long hydrophobic tail, where the polar head is a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as may be measured by JIS K2501) of from 0 to 80. It is possible to include large amounts of a metal base by reacting an excess of a metal compound such as an oxide or hydroxide with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically of from 250 to 450 or more.

Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the alkali metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about 100 to 220 wt % of that stoichiometrically required.

Metal salts of alkyl phenols and sulfurized alkyl phenols are prepared by reaction with an appropriate metal compound such as an oxide, hydroxide or alkoxide and overbased products may be obtained by methods well known in the art. Sulfurized alkyl phenols may be prepared by reacting an alkyl phenol with sulfur or a sulfur containing compound such as hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur containing bridges.

Metal salts of carboxylic acids (including salicylic acids) may be prepared in a number of ways: for example, by adding a basic metal

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compound to a reaction mixture comprising the carboxylic acid (which may be part of a mixture with another organic acid such as a sulfonic acid) or its metal salt and promoter, and removing free water from the reaction mixture to form an metal salt, then adding more basic metal compound to the reaction mixture and removing free water from the reaction mixture. The carboxylate is then overbased by introducing the acidic material such as carbon dioxide to the reaction mixture while removing water. This can be repeated until a product of the desired TBN is obtained.

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The overbasing process is well known in the art and typically comprises reacting acidic material with a reaction mixture comprising the organic acid or its metal salt, a metal compound. That acidic material may be a gas such as carbon dioxide or sulfur dioxide, or it may be boric acid. Processes for the preparation of overbased alkali metal sulfonates and phenates are described in EP-A-266034. A process suitable for overbased sodium sulfonates is described in EP-A-235929. A process for making overbased salicylates is described in EP-A-351052.

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The overbased metal detergents can be borated. The boron may be introduced by using boric acid as the acidic material used in the overbasing step. However an alternative is to borate the overbased product after formation by reacting a boron compound with the overbased metal salt. Boron compounds include boron oxide, boron oxide hydrate, boron trioxide, boron trifluoride, boron tribromide, boron trichloride, boron acid such as boronic acid, boric acid, tetraboric acid and metaboric acid, boron hydrides, boron amides and various esters of boron acids. Boric acid is preferred. Generally, the overbased metal salt may be reacted with a boron compound at from 50°C to 250°C, in the presence of a solvent such as mineral oil or xylene.

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Conveniently, the lubricant composition of the present invention contains an overbased metal detergent in an amount sufficient to provide a total base value of the finished lubricant in the range from about 3 to about 10, more preferably from 4 to 7. The total base value can be

measured according to JIS K2501. The total base value can be adjusted preferably by selecting a metal detergent with an appropriate base value.

If desired, an ashless dispersant may be blended into the lubricant. The ashless dispersant comprises an oil solubilizing polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, the dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often via a bridging group. The ashless dispersant may be, for example, selected from oil soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

The oil soluble polymeric hydrocarbon backbone is typically an olefin polymer, especially polymers comprising a major molar amount (i.e. greater than 50 mole %) of a C₂ to C₁₈ olefin (e.g., ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene), and typically a C₂ to C₅ olefin. The oil soluble polymeric hydrocarbon backbone may be a homopolymer (e.g. polypropylene or polyisobutylene) or a copolymer of two or more of such olefins (e.g. copolymers of ethylene and an alpha-olefin such as propylene and butylene or copolymers of two different alpha-olefins). Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole %, is a C₃ to C₂₂ non-conjugated diolefin (e.g., a copolymer of isobutylene and butadiene, or a copolymer of ethylene, propylene and 1,4-hexadiene or 5-ethylidene-2-norbornene). One preferred class of olefin polymers is polybutenes and specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C₄ refinery stream.

The oil soluble polymeric hydrocarbon backbone will usually have number average molecular weight (\bar{M}_n) within the range of from 300 to 20,000, conveniently 500 to 10,000, and usually 700 to 5,000.

Particularly useful olefin polymers for use in dispersants have \bar{M}_n within the range of from 1500 to 3000. The \bar{M}_n for such polymers can be determined by several known techniques. A convenient method for such determination is by gel permeation chromatography which additionally provides molecular weight distribution information, see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979.

The oil soluble polymeric hydrocarbon backbone may be functionalized to incorporate a functional group into the backbone of the polymer, or as one or more groups pendant from the polymer backbone. The functional group typically will be polar and contain one or more hetero atoms such as P, O, S, N, halogen, or boron. It can be attached to a saturated hydrocarbon part of the oil soluble polymeric hydrocarbon backbone via substitution reactions or to an olefinic portion via addition or cycloaddition reactions. Alternatively, the functional group can be incorporated into the polymer in conjunction with oxidation or cleavage of the polymer chain end (e.g., as in ozonolysis).

Useful functionalization reactions include: halogenation of the polymer at an olefinic bond and subsequent reaction of the halogenated polymer with an ethylenically unsaturated functional compound; reaction of the polymer with an unsaturated functional compound by the "ene" reaction absent halogenation (e.g., maleation where the polymer is reacted with maleic acid or anhydride); reaction of the polymer with at least one phenol group (this permits derivatization in a Mannich base-type condensation); reaction of the polymer with the functionalizing compound by free radical addition using a free radical catalyst; reaction with a thiocarboxylic acid derivative; and reaction of the polymer by air oxidation methods, epoxidation, chloroamination, or ozonolysis.

The functionalized oil soluble polymeric hydrocarbon backbone is then further derivatized with a nucleophilic reactant such as an amine, amino-alcohol, alcohol, metal compound or mixture thereof to form a corresponding derivative. Useful amine compounds for derivatizing functionalized polymers comprise at least one amine and can comprise

one or more additional amine or other reactive or polar groups. These amines may be hydrocarbyl amines or may be predominantly hydrocarbyl amines in which the hydrocarbyl group includes other groups, e.g., hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline 5 groups, and the like. Particularly useful amine compounds include mono- and polyamines, e.g. polyalkylene and polyoxyalkylene polyamines of about 2 to 60, conveniently 2 to 40 (e.g., 3 to 20), total carbon atoms and about 1 to 12, conveniently 3 to 12, and 3 to 9 nitrogen atoms in the molecule.

10 The functionalized oil soluble polymeric hydrocarbon backbones also may be derivatized with hydroxy compounds such as monohydric and polyhydric alcohols or with aromatic compounds such as phenols and naphthols.

15 A preferred group of ashless dispersants includes those substituted with succinic anhydride groups and reacted with polyethylene amines (e.g., tetraethylene pentamine), aminoalcohols such as trismethylolaminomethane and optionally additional reactants such as alcohols and reactive metals e.g., pentaerythritol, and combinations thereof). Also useful are dispersants wherein a polyamine is attached 20 directly to the backbone by the methods shown in US 3,275,554 and 3,565,804 where a halogen group on a halogenated hydrocarbon is displaced with various alkylene polyamines.

25 Another class of ashless dispersants comprises Mannich base condensation products. Generally, these are prepared by condensing about one mole of an alkyl-substituted mono- or polyhydroxy benzene with about 1 to 2.5 moles of carbonyl compounds (e.g., formaldehyde and paraformaldehyde) and about 0.5 to 2 moles polyalkylene polyamine as disclosed, for example, in US 3,442,808. Such Mannich condensation products may include a long chain, high molecular weight hydrocarbon 30 (e.g., \bar{M}_n of 1,500 or greater) on the benzene group or may be reacted with a compound containing such a hydrocarbon, for example, polyalkenyl succinic anhydride as shown in US 3,442,808.

The functionalizations, derivatizations, and post-treatments described in the following patents may also be adapted to functionalize and/or derivatize the preferred polymers described above: US 3,275,554, 3,565,804, 3,442,808, 3,442,808, 3,087,936 and 3,254,025.

5 The dispersant can be further post-treated by a variety of conventional post treatments such as boration, as generally taught in US 3,087,936 and 3,254,025. This is readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from the group consisting of boron oxide, boron halides, boron acids and esters of boron acids, in an amount to provide from about 0.1 atomic proportion of boron for each mole of the acylated nitrogen composition to about 20 atomic proportions of boron for each atomic proportion of nitrogen of the acylated nitrogen composition. The boron, which appears 10 be in the product as dehydrated boric acid polymers (primarily $(\text{HBO}_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts e.g., the metaborate salt of the diimide. Boration is readily carried out by adding from about 0.05 to 4, e.g., 1 to 3 wt. % (based on the weight of 15 acyl nitrogen compound) of a boron compound, preferably boric acid, usually as a slurry, to the acyl nitrogen compound and heating with stirring at from 135° to 190° C, e.g., 140°-170° C, for from 1 to 5 hours followed by nitrogen stripping. Alternatively, the boron treatment can be 20 carried out by adding boric acid to a hot reaction mixture of the dicarboxylic acid material and amine while removing water.

25 When the dispersant is a nitrogen containing dispersant, the ratio of the number of boron atoms/the number of nitrogen atoms in the boron containing succinimide to be used in the lubricant composition of the present invention is 0.05 to 1.5, preferably 0.1 to 0.8. If the ratio of the number of boron atoms/the number of nitrogen atoms is below 0.05, satisfactory improvement of friction properties (low friction) cannot be 30 brought about; if the ratio of the number of boron atoms/the number of nitrogen atoms is above 1.5, friction properties are deteriorated.

In the lubricant composition of the present invention, the boron containing succinimide should be blended at an amount such that the

boron content from boron containing succinimide is at 0.005 to 0.06 % by weight, preferably 0.01 to 0.04 % by weight to the total weight of the composition. When the boron containing succinimide is blended at an amount such that the boron content from boron containing succinimide is below 0.005 % by weight to the total weight of the composition, no satisfactory improvement of friction properties (low friction) can be brought about; if the boron containing succinimide is blended at an amount such that the boron content from boron containing succinimide is above 0.06 % by weight to the total weight of the composition, no improvement of the effect can be brought about in proportion to the amount.

In a range without departing from the scope of the present invention, various additives conventionally used for lubricants, for example, other friction modifiers, other metal detergents, other wear preventing agents, antioxidants, viscosity modifiers, pour point decreasing agents, anti-foaming agents, rust preventive agents, and corrosion inhibitors, may be blended in the lubricant composition of the present invention.

Other friction modifiers include for example polyhydric alcohol partial ester, amine, amide, sulfide ester and the like. Boration of friction modifiers is well known in the art and represents an alternative way to introduce boron into the lubricant.

Other metal detergents include for example barium sulfonate, barium phenate and the like, which may be used generally at a ratio of 0.1 to 5 % by weight.

Other wear preventing agents include for example thiophosphate metal salt, sulfur compound, phosphate ester, phosphite ester and the like, which may be used generally at a ratio of 0.05 to 5.0 % by weight.

Antioxidants include for example amine antioxidants such as alkylated diphenylamine, phenyl- α -naphthylamine, and alkylated α -naphthylamine; and phenol antioxidants such as 2,6-di-t-butyl-4-methyl

phenol and 4,4'-methylene-bis(2,6-di-t-butyl phenol), which may be used generally at a ratio of 0.05 to 4 % by weight.

Viscosity modifiers (also frequently called viscosity index improvers) include for example polymethacrylates, polyisobutylenes, ethylene-propylene copolymers, styrene-butadiene hydrogenated copolymers and the like, which may be used generally at a ratio of 0.5 to 5
35 % by weight.

Pour point decreasing agents include for example polyalkylmethacrylate, chlorinated paraffin-naphthalene condensed product, alkylated polystyrene and the like.

Anti-foaming agents include for example dimethylpolysiloxane, polyacrylic acid and the like.

Rust preventing agents include for example fatty acid, alkenyl succinate partial ester, fatty acid soap, alkylsulfonate salt, fatty acid polyhydric alcohol ester, fatty acid amine, paraffin oxide, alkylpolyoxyethylene ether and the like.

Corrosion inhibitors include for example benzotriazole and benzoimidazole.

Examples

The present invention will now be explained in detail in examples, but the invention is not limited to these examples.

Herein, the coefficient of friction of the lubricant composition was measured at a 50-Hz frequency, a 3 mm amplitude, a 25-N load, a 25 temperature of 80°C and a testing period of 25 minutes, using a reciprocate dynamic sliding friction tester (SRV friction tester).

The oxidation test by means of air containing gaseous nitrogen oxides was carried out using a 150 ml test oil at a temperature of 130°C, a nitrogen oxide level of 1 % by volume, a flow of 2 liters/hour, and a 30 testing period of 8 hours.

Examples 1 to 9 and Comparative Examples 1 and 2

Examples 1 to 9 are lubricant compositions blended with (A) oxymolybdenum dithiocarbamate sulfide, (B) zinc dialkyldithiophosphate, (C) zinc dialkyldithiocarbamate, copper dialkyldithiocarbamate, 5 bis(dialkylthiocarbamoyl)disulfide or dibenzylidisulfide, (D) calcium salicylate, and (E) boron containing succinimide. Furthermore, Comparative Examples A and B are lubricant compositions containing the components (A), (B), (D) and (E), without containing the component (C).

10 Individual components of a type and an amount shown in Table 1 were blended with the base oil (100 Neutral Oil with a viscosity of 4.4 mm/s² at 100°C) to prepare lubricant compositions containing the components, and the coefficient of friction immediately after the preparation was measured, together with the coefficient of friction after the preparations were stored and oxidized in the presence of gaseous nitrogen oxides at 130°C for 8 hours. The results are shown in Table 1.

15 All the lubricant compositions of Examples 1 to 9 all have good friction properties with low coefficients of friction. No change in the coefficients of friction was observed even after the lubricant compositions were heated in the presence of gaseous nitrogen oxides at 130°C for 8 hours. Thus, it is indicated that these lubricant compositions have good resistance to oxidation with no change in the observed coefficients of friction. Alternatively, the lubricant compositions of Comparative Examples A and B, without containing the component (C), i.e., a sulfur compound, have low coefficients of friction immediately after preparation, 20 but have acquired higher coefficients of friction after the preparations were heated and oxidized in the presence of gaseous nitrogen oxides at 130°C for 8 hours, indicating that their resistance to oxidation is poor.

25 The lubricant composition of the present invention has acquired good low abrasion property, through the blending of a lubricant base oil with oxymolybdenum dithiocarbamate sulfide, zinc dialkyldithiophosphate, and a sulfur compound, each having a specific structure, a metal detergent and boron containing succinimide. The composition can sustain good friction properties (low friction) while exhibiting resistance to

oxidation at higher temperatures in the presence of gaseous nitrogen oxides, and is preferably used as lubricants for internal combustion engines, automatic transmission, snubbers, and power steering, preferably for internal combustion engines in particular.

	Example						Comp. Example				
	1	2	3	4	5	6	7	8	9	A	B
Mo from C ₈ -MoDTC (ppm)	600	600	400		600	600	600	600	600	600	
Mo from C ₁₃ -MoDTC (ppm)				600							600
P from C ₈ -ZnDTP (wt %)	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
S from C ₅ -ZnDTC (wt %)	0.15	0.05	0.10	0.10	0.10						
S from C ₄ -CuDTC (wt %)						0.05					
S from bis(dialkylthiocarbamoyl)disulfide (wt %)							0.10				
S from dibenzylsulfide (wt %)								0.10			
Calcium salicylate (wt %)	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Boron containing succinimide (wt %, ≈ 50 % active ingredient in oil)	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
Coefficient of friction (immediately after preparation)	0.087	0.087	0.090	0.089	0.094	0.094	0.092	0.085	0.086	0.086	0.091
Coefficient of friction (after oxidation with NO _x at 130°C for 8 hrs)	0.090	0.091	0.094	0.095	0.097	0.101	0.095	0.087	0.094	0.167	0.175

NOTE:

- C₈-MoDTC: Oxyomolybdenum-N,N-diethylthiocarbamate sulfide
- C₁₃-MoDTC: Oxyomolybdenum-N,N-ditridecylthiocarbamate sulfide
- C₈-ZnDTP (primary): zinc-di-2-ethylhexylthiophosphate
- C₅-ZnDTL: zinc diaryldithiocarbamate
- C₄-CuDTC: copper dibutylthiocarbamate

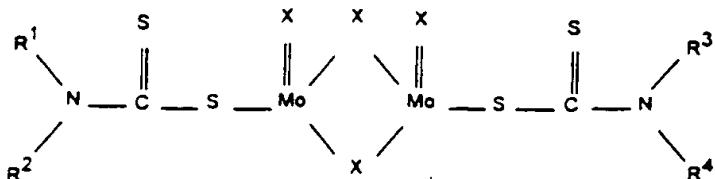
CLAIMS:

1. A lubricant composition comprising a major amount of an oil of lubricating viscosity having added thereto a minor amount of additives comprising
 - (A) oxymolybdenum dithiocarbamate sulfide having alkyl groups with 8 to 18 carbon atoms,
 - (B) zinc dialkyldithiophosphate having primary alkyl groups with 1 to 18 carbon atoms,
 - (C) one or more additional peroxide decomposing sulfur compounds,
 - (D) an ashless dispersant, and
 - (E) a boron containing additivewherein to the total weight of the composition, the molybdenum content from oxymolybdenum dithiocarbamate sulfide is at 200 to 2,000 ppm (ratio by weight); the phosphorous content from zinc dialkyldithiophosphate is from 0.02 to 0.15 % by weight; the sulfur content from the additional sulfur compounds is from 0.02 to 0.30 % by weight, and the boron content is from 0.005 to 0.06 % by weight.
- 20 2. The lubricant of claim 1 wherein the one or more additional peroxide decomposing sulfur compounds is selected from the group consisting of zinc dialkyldithiocarbamate, copper dialkyldithiocarbamate or nickel dialkyldithiocarbamate wherein the dialkyldithiocarbamate has alkyl groups with 2 to 18 carbon atoms, bis(dialkylthiocarbamoyl)disulfide having alkyl groups with 2 to 18 carbon atoms, disulfide having alkyl groups, allyl groups, alkylallyl groups, or an allylalkyl groups, with 6 to 18 carbon atoms, olefin sulfide, fish oil sulfide, whale oil sulfide, and mixtures of any of the foregoing.
- 30 3. The lubricant of claim 1 further comprising (F) from 1 to 10 % by weight of one or more metal detergents selected from the group consisting of calcium salicylate, magnesium salicylate, calcium sulfonate, magnesium sulfonate and calcium phenate.
4. The lubricant composition of claim 1 wherein the ashless dispersant and boron containing additive are a borated polyalkenyl succinimide.

5. A lubricant composition comprising a major amount of a lubricant base oil, and a minor amount of additives comprising (A) oxymolybdenum dithiocarbamate sulfide having alkyl groups with 8 to 18 carbon atoms, (B) zinc dialkyldithiophosphate having primary alkyl group with 1 to 18 carbon atoms, and (C) one or more additional sulfur components selected from the group consisting of zinc dialkyldithiocarbamate, copper dialkyldithiocarbamate or nickel dialkyldithiocarbamate, having alkyl groups with 2 to 18 carbon atoms, bis(dialkylthiocarbamoyl)disulfide having alkyls group with 2 to 18 carbon atoms, disulfide having alkyl groups, allyl groups, alkylallyl groups or allylalkyl groups, with 6 to 18 carbon atoms, olefin sulfide, fish oil sulfide and whale oil sulfide, and (D& E) boron containing succinimide, (F) one or more metal detergents selected from the group consisting of calcium salicylate, magnesium salicylate, calcium sulfonate, magnesium sulfonate and calcium phenate, wherein to the total weight of the composition, the molybdenum content from oxymolybdenum dithiocarbamate sulfide is from 200 to 2,000 ppm (ratio by weight); the phosphorous content from zinc dialkyldithiophosphate is from 0.02 to 0.15 % by weight; the sulfur content from sulfur compounds is from 0.02 to 0.30 % by weight; the content of a metal detergent is from 1 to 10 % by weight; and the boron content from boron containing succinimide is from 0.005 to 0.06 % by weight.

6. The composition of claim 2 wherein the oxymolybdenum dithiocarbamate is of the formula

25



wherein R¹, R², R³ and R⁴ may be the same or different, each representing an alkyl group with 8 to 13 carbon atoms and X represents S or O.

30 7. The composition of claim 2 wherein the zinc dialkyldithiophosphat has primary alkyl groups with 3 to 12 carbon atoms.

8. The composition of claim 3 wherein the ratio of the number of boron atoms to the number of nitrogen atoms in the boron containing succinimide is 0.05 to 1.5.

5 9. The composition of claim 1 wherein the additional sulfur containing compound is dibenzyl disulfide.

10. The composition of claim 3 wherein the metal detergent is calcium salycilate.

INTERNATIONAL SEARCH REPORT

Int. Appl. No.
PCT/IB 95/00725

A. CLASSIFICATION OF SUBJECT MATTER
**IPC 6 C10M141/10 C10M163/00 C10M141/12 // (C10M141/10, 133:56,
 135:04, 135:06, 135:18, 135:22, 135:28, 137:10), (C10M163/00, 133:56,
 135:04, 135:06, 135:18, 135:22, 135:28, 137:10, 139:00, 159:22, 159:24),**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 588 561 (ORONITE JAPAN LIMITED) 23 March 1994 see page 2, line 18 - line 36 see page 7, line 15 - line 36 see page 8, line 43 - line 46 ----	1-8
Y	EP,A,0 113 045 (IDEMITSU KOSAN COMPANY LIMITED) 11 July 1984 see page 12, line 13 - line 16; claims 1,8,9 ----	1-8
A	EP,A,0 562 172 (IDEMITSU KOSAN COMPANY) 29 September 1993 see page 3, line 53 - line 54; claims 1,5,6 see page 5; table 1 ----	1,3-6,8, 10 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
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- 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- '&' document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 November 1995	24-11-1995

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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P,A	WO,A,94 28095 (EXXON RESEARCH AND ENGINEERING COMPANY) 8 December 1994 see the whole document ----	1,3-7,10
A	EP,A,0 281 992 (IDEMITSU KOSAN COMPANY LIMITED) 14 September 1988 ----	
A	US,A,4 648 985 (P.W. THORSELL) 10 March 1987 -----	

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PCT/IB 95/00725	

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